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# Optical absorption spectrum and local symmetry of $Tm^{3+}$ ion in $TmAl_3(BO_3)_4$ crystal

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## Abstract

With the help of group theory analysis of absorption spectra of the transition $^3H_6 \to {}^3F_3$ of $Tm^{3+}$ ion in $TmAl_3(BO_3)_4$ crystal, measured at several temperatures from 1.8 till 293 K, it has been shown, that the local symmetry of the $Tm^{3+}$ environment is $C_3$ and it decreases to $C_1$ at a low temperature. Effective selection rules and polarizations of lines at high enough temperatures (when the line-width is larger than the splitting in $C_3$ symmetry) have been obtained.

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*Keywords:* Rare earth compounds; Spectroscopy; Site symmetry

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The $TmAl_3(BO_3)_4$ crystals have huntite type structure [1] with the space group R32 (No. 155 of the International Tables for X-Ray Crystallography). The unit cell contains three formula units ($Z = 3$). Trivalent rare-earth (RE) ions occupy only one type positions. This circumstance is one of the advantages of the crystal, making the interpretation of spectral information to be more reliable. A number of works are known devoted to spectroscopic properties of RE ions in similar crystals in connection with their application in laser technique (e.g., [2–6]). The local symmetry of RE ion positions was supposed to be $D_3$ [2–4]. In this work we present arguments, that the local symmetry of $Tm^{3+}$ ions in the studied crystal is lower.

Single crystals of $TmAl_3(BO_3)_4$ were grown from a melt solution [7]. High-resolution absorption spectra were measured in the region of $^3H_6 \to {}^3F_3$ transition at several temperatures from 1.8 till 293 K. Some of the spectra are shown in Figs. 1, 2 and 3. The spectra were decomposed into Gaussian components, and parameters of the absorption lines (intensity, position and width) were obtained (Table 1). Lines No. 1–12 are observed only at high temperatures. All lines, beginning from 11, are not indicated on the spectra at 293 K in Fig. 1, since this part of the spectra is a superposition of many lines, as it is seen from the low temperature spectra (Figs. 2 and 3). Lines 10–12 are well resolved at 80 K (insert to Fig. 1), and their parameters are given in Table 1 for $T = 80$ K. The parameters of lines No. 1–9 are given for 293 K, and the parameters of lines 13–30 are given for 1.8 K.

Thulium ions, like the other RE ions in the huntite structure, are surrounded by six crystallographically equivalent oxygen ions, forming trigonal prism [8], and the local symmetry, by analogy with the same crystal with Tb, Nd and Pr [2–4], is originally supposed to be $D_3$. The group $D_3$ is subgroup of cubic $O$ group (indeed, trigonal prism is a distorted octahedron). In non-centrosymmetric $D_3$ and $O$ groups $f{-}f$ transitions are already parity allowed. It is primarily static distortions rather than

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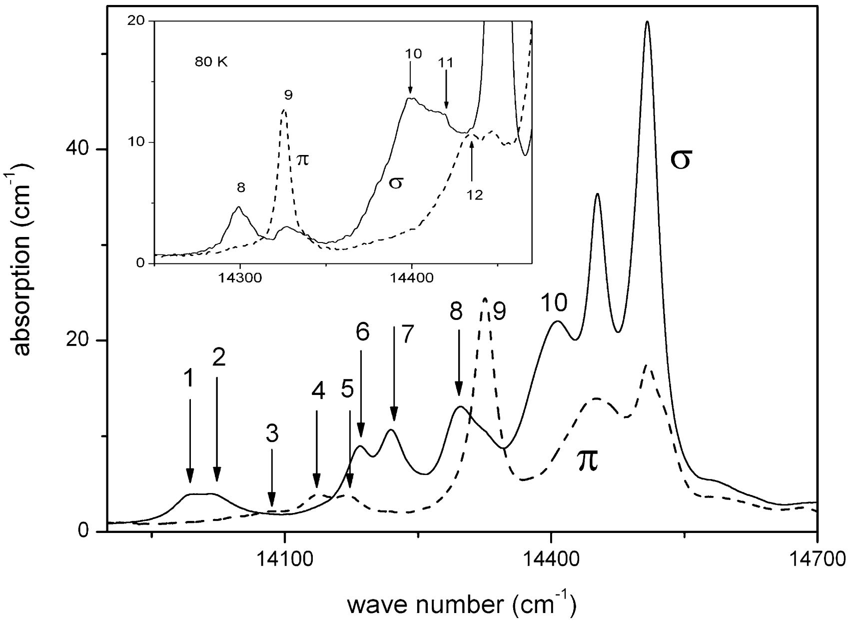

Fig. 1. Absorption $\pi$ and $\sigma$ spectra in the region of $^3H_6 \rightarrow {}^3F_3$ transition at $T = 293$ K. Inset: part of the absorption spectra at 80 K.

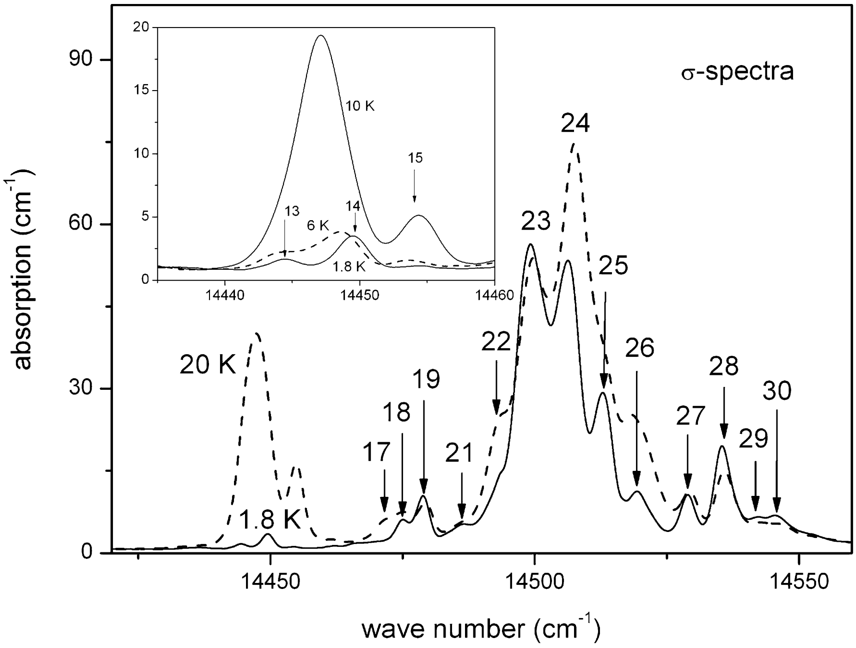

Fig. 2. $\sigma$-polarized absorption spectra in the region of $^3H_6 \rightarrow {}^3F_3$ transition at several low temperatures.

vibrations that usually lift forbiddenness from the $f$–$f$ transitions [9]. In order to interpret the spectra obtained, we consider the splitting of states (and the corresponding absorption lines) in two steps: first, the splitting of states in the crystal field (CF) of the cubic symmetry, and then, further splitting of states in the trigonal CF. In $O$ symmetry only magnetic dipole transitions are allowed, since only their functions present among bases functions of $O$ group [10]. On the same reason, in $D_3$ symmetry only $z$ ($\pi$) polarized electric dipole transitions are allowed, but in $C_3$ group (subgroup of $D_3$) all polarizations are allowed. Simultaneously, in the $C_3$ group all degenerations of states are lifted [10]. In our experimental spectra (Figs. 1, 2, 3 and Table 1) absorption lines of both polarizations are observed. This means that the local symmetry should be lower than $D_3$. Therefore we consider the splitting schemes for the ground and excited states in the cubic $O$, trigonal $D_3$ and $C_3$ CF, successively [10]:

$$\begin{aligned} J = 6\big({}^3H_6\big) &\in \Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5 \\ &\in \gamma_1(\gamma_1) + \gamma_2(\gamma_1) + \gamma_3(\gamma_2+\gamma_3) + \big[\gamma_2(\gamma_1) + \gamma_3(\gamma_2+\gamma_3)\big] + 2\big[\gamma_1(\gamma_1) + \gamma_3(\gamma_2+\gamma_3)\big], \end{aligned} \tag{1}$$

$$J = 3\big({}^3F_3\big) \in \Gamma_2 + \Gamma_4 + \Gamma_5 \in \gamma_2(\gamma_1) + \big[\gamma_2(\gamma_1) + \gamma_3(\gamma_2+\gamma_3)\big] + \big[\gamma_1(\gamma_1) + \gamma_3(\gamma_2+\gamma_3)\big]. \tag{2}$$

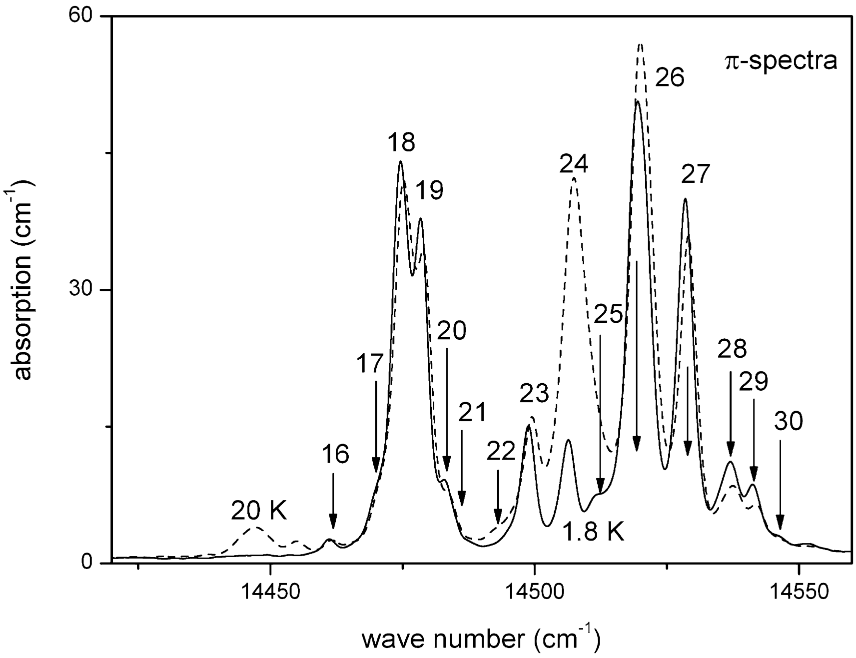

Fig. 3. $\pi$-polarized absorption spectra in the region of $^3H_6 \rightarrow {}^3F_3$ transition at several low temperatures.

Table 1
Wave numbers ($k$), intensities ($I$) and line widths ($\Delta k$) of absorption lines in $\pi$ and $\sigma$ polarizations. Parameters of lines No. 1–9 are given for $T = 293$ K, No. 10–12 for 80 K and No. 13–30 for 1.8 K

| | $\pi$ | | | $\sigma$ | | |
|---|---|---|---|---|---|---|
| | $k$ (cm$^{-1}$) | $I$ (cm$^{-2}$) | $\Delta k$ (cm$^{-1}$) | $k$ (cm$^{-1}$) | $I$ (cm$^{-2}$) | $\Delta k$ (cm$^{-1}$) |
| 1 | – | – | – | 13993.4 | 86 | 41.8 |
| 2 | – | – | – | 14022.2 | 69 | 43.3 |
| 3 | 14089.1 | 106 | 106 | – | – | – |
| 4 | 14136.9 | 93 | 44 | – | – | – |
| 5 | 14171.9 | 66 | 39 | – | – | – |
| 6 | – | – | – | 14184.1 | 197 | 33.6 |
| 7 | – | – | – | 14217.8 | 183 | 29.7 |
| 8 | – | – | – | 14295.1 | 438 | 40.9 |
| 9 | 14326 | 577 | 27.4 | 14329.3 | 324 | 43.8 |
| 10 | – | – | – | 14399 | 248 | 24.9 |
| 11 | – | – | – | 14420.3 | 238 | 22.2 |
| 12 | 14433.5 | 133 | 15.3 | – | – | – |
| 13 | – | – | – | 14444 | 3.8 | 7.5 |
| 14 | – | – | – | 14449 | 7.0 | 3.8 |
| 15 | – | – | – | 14454 | 2.8 | 7.5 |
| 16 | 14461.3 | 9.4 | 5.6 | 14461.5 | 2.1 | 2.8 |
| 17 | 14470.7 | 41.3 | 5.6 | – | – | – |
| 18 | 14474.6 | 157 | 3.5 | 14475.3 | 17.6 | 3.8 |
| 19 | 14478.8 | 115 | 2.8 | 14479.0 | 24.6 | 3.8 |
| 20 | 14483 | 32.1 | 4.2 | – | – | – |
| 21 | 14487.2 | 15.6 | 13.3 | 14486.6 | 35.8 | 8.8 |
| 22 | 14494 | 32.6 | 7.0 | 14492.8 | 50.2 | 6.3 |
| 23 | 14499.1 | 30.4 | 2.8 | 14499.1 | 331 | 6.3 |
| 24 | 14506.1 | 49.7 | 3.5 | 14506.6 | 342 | 6.3 |
| 25 | 14512.5 | 41.9 | 5.6 | 14512.8 | 110 | 3.8 |
| 26 | 14519.5 | 271 | 4.9 | 14519.1 | 74.8 | 7.5 |
| 27 | 14528.7 | 166 | 4.2 | 14529.1 | 40.2 | 3.8 |
| 28 | 14537.1 | 63.5 | 6.3 | 14535.7 | 66.6 | 3.5 |
| 29 | 14542.1 | 16 | 2.8 | 14542.1 | 28.2 | 4.2 |
| 30 | 14545.6 | 9.4 | 4.9 | 14545.6 | 26.4 | 4.2 |

Letters $\Gamma_n$ denote representations in the cubic symmetry and $\gamma_n$ denote representations in the $D_3$ and $C_3$ symmetries. $\gamma_3$ is twofold representation in the $D_3$ group. The states, corresponding to the $C_3$ symmetry are in round brackets.

In order for a transition to be allowed, the representation of the transition operator

$$\Gamma_t = \Gamma_i \Gamma_f, \tag{3}$$

where $\Gamma_i$ and $\Gamma_f$ are representations of the initial and final states, respectively, should contain the representation of the electric dipole moment $\Gamma_d$: $\gamma_2$ for $\pi$-polarization in the $D_3$ group, or $\gamma_1$ for $\pi$-polarization and $\gamma_2$ or $\gamma_3$ for $\sigma$-polarization in the $C_3$ group [10]. Taking into account (1), (2) and (3), and with the help of tables [10], we obtain the following transitions in $C_3$ symmetry from the components of the ground state splitting in the cubic CF:

$$\Gamma_1 \to \Gamma_2[\pi] + \Gamma_4\big[\pi + (2\sigma)\big] + \Gamma_5(\pi + 2\sigma), \tag{4}$$

$$\Gamma_2 \to \Gamma_2(\pi) + \Gamma_4(\pi + 2\sigma) + \Gamma_5\big[\pi + (2\sigma)\big], \tag{5}$$

$$\Gamma_3 \to \Gamma_2(2\sigma) + \Gamma_4\big[2\pi + (4\sigma)\big] + \Gamma_5\big[2\pi + (4\sigma)\big], \tag{6}$$

$$\begin{aligned}\Gamma_4 \to {} & \Gamma_2\left[\frac{\gamma_2 - \gamma_2}{(\pi)} + \frac{\gamma_3 - \gamma_2}{(2\sigma)}\right] + \Gamma_4\left[\frac{\gamma_2 - \gamma_2}{(\pi)} + \frac{\gamma_2 - \gamma_3}{(2\sigma)} + \frac{\gamma_3 - \gamma_2}{(2\sigma)} + \frac{\gamma_3 - \gamma_3}{(2\sigma) + 2\pi}\right] \\ & + \Gamma_5\left[\frac{\gamma_2 - \gamma_1}{\pi} + \frac{\gamma_2 - \gamma_3}{(2\sigma)} + \frac{\gamma_3 - \gamma_1}{(2\sigma)} + \frac{\gamma_3 - \gamma_3}{(2\sigma) + 2\pi}\right],\end{aligned} \tag{7}$$

$$\begin{aligned}\Gamma_5 \to {} & \Gamma_2\left[\frac{\gamma_1 - \gamma_2}{\pi} + \frac{\gamma_3 - \gamma_2}{(2\sigma)}\right] + \Gamma_4\left[\frac{\gamma_1 - \gamma_2}{\pi} + \frac{\gamma_1 - \gamma_3}{(2\sigma)} + \frac{\gamma_3 - \gamma_2}{(2\sigma)} + \frac{\gamma_3 - \gamma_3}{(2\sigma) + 2\pi}\right] \\ & + \Gamma_5\left[\frac{\gamma_1 - \gamma_1}{(\pi)} + \frac{\gamma_3 - \gamma_1}{(2\sigma)} + \frac{\gamma_1 - \gamma_3}{(2\sigma)} + \frac{\gamma_3 - \gamma_3}{(2\sigma) + 2\pi}\right].\end{aligned} \tag{8}$$

Decompositions for the transitions from $\Gamma_4$ and $\Gamma_5$ manifolds of $J = 6$ multiplet are shown in detail. Letters $\gamma_n$ denote here representations only in the $D_3$ symmetry. Polarization and number of corresponding lines in $C_3$ symmetry for the transitions from $\Gamma_4$ and $\Gamma_5$ manifolds are shown in denominators. The transitions forbidden in $D_3$ symmetry are shown in the round brackets. In $C_3$ symmetry not only all degenerations are lifted, but also all possible transitions between components of the splitting are electric dipole allowed. At the lowest temperature used (1.8 K) only one of the sublevels of the ground state splitting in the cubic CF can be occupied and, as a consequence, only one of the above sets of the transitions can be observed. The problem is to find, what of the sublevels is the lowest one.

In our spectra at 1.8 K, 18 lines are observed in both polarizations. From (7) and (8) it is seen, that in the $D_3$ symmetry, only 10 transitions are possible from the $\Gamma_4$ and $\Gamma_5$ manifolds, and only 5 and 6 of them, respectively from the $\Gamma_4$ and $\Gamma_5$, are electric dipole allowed, and in $\pi$-polarization only. According (4)–(8), 21 transitions are possible (and allowed) in $C_3$ symmetry from the manifolds $\Gamma_4$ and $\Gamma_5$ and only 14 or less ones from other manifolds. This means, that sublevels of the $\Gamma_4$ and $\Gamma_5$ states of the ground multiplet are candidates for the lowest level, and that the local symmetry of the $Tm^{3+}$ environment is lower than $D_3$. Number of experimentally observed transitions can be less than the theoretical one from the $\Gamma_4$ and $\Gamma_5$ states, since the splitting in $C_3$ can be too small for observation and frequencies of some lines can coincide. From (4)–(8) it follows that all lines should be totally polarized in $C_3$ symmetry, but in the experiment at low temperatures majority of lines are observed in both polarizations (see Figs. 2, 3 and Table 1). This is possible only in $C_1$ symmetry; however, such lowering of the symmetry does not give additional splitting, since all degenerations were already lifted in the $C_3$ symmetry.

Absorption lines, observed at 1.8 K, are separated into two groups. Intensity of 13 lines (No. 16–21, 23, 25–30) does not change or decreases with the increasing temperature (group "a"), and intensity of 5 lines (No. 13–15, 22, 24) strongly increases with the increasing temperature in the low temperature interval (group "b") (see Fig. 2). This means, that the former transitions occur from the lowest sublevels of $\Gamma_4$ (or $\Gamma_5$) manifold of the cubic classification and the latter ones—from the upper sublevels. The line No. 17 reveals a peculiar behavior. At 1.8 K it is observed only in $\pi$-polarization and does not increase with temperature rising, but in $\sigma$-polarization it appears and increases at $T > 1.8$ K. This can be connected with structural distortions. (Detail study of temperature transformation of the spectra is in progress.)

From (7) and (8) it is evident, that in $C_3$ symmetry 14 transitions are possible and allowed from $\gamma_3$ ($D_3$ label) sublevels of $\Gamma_4$ and $\Gamma_5$ manifolds, and 7 transitions are possible and allowed from $\gamma_2$ or $\gamma_1$ ($D_3$ labels) sublevel of $\Gamma_4$ or $\Gamma_5$ manifolds, respectively. Thus, above mentioned 13 absorption lines of the group "a" can be assigned to the transitions from the lowest sublevels $\gamma_3$ ($D_3$ label) and 5 lines of the group "b"—to the transitions from the next sublevel $\gamma_2$ or $\gamma_1$ ($D_3$ labels) of $\Gamma_4$ or $\Gamma_5$ manifolds, respectively. Mutual position of low energy lines of groups "a" and "b" confirms the assignment of mutual position of the corresponding initial states. Distance between these lines: $\sim 17\ \text{cm}^{-1}$ is the splitting between $\gamma_3$ and $\gamma_2$ ($\gamma_1$) states (in $D_3$ symmetry). Additional splitting of $\gamma_3$ state due to $C_3$ distortion is of the order of units of $\text{cm}^{-1}$. The $C_1$ symmetry distortion only a little changes values of splitting and depolarize the transitions. Distance between lines No. 1 and 16, i.e. distance between low energy lines observed at 293 K and at 1.8 K (group "a"), gives, evidently, the overall CF splitting of the ground state $^3H_6$ . It is equal to $468\ \text{cm}^{-1}$. Distance between the first and the last lines of the group "a", $84\ \text{cm}^{-1}$, estimates the overall CF splitting of the excited state.

It is evident, that the value of splitting of states (and transitions) is mainly due to the cubic and $D_3$ components of CF. At the same time, from (7) and (8) it is seen, that existence and polarization of the transitions are conditioned by the $C_3$ symmetry distortion. In the $C_3$ symmetry all transitions are totally polarized. At high enough temperature, when line-widths are much larger than the additional splitting in $C_3$ symmetry, it is possible to neglect small splitting of states by $C_3$ distortion, and observed spectra will correspond to splitting in $D_3$ symmetry. However, effective selection rules and polarizations of such lines are governed by $C_3$ distortion and follow from (7) and (8). Here they are (in terms of $D_3$ group): ($\gamma_1$–$\gamma_2$), ($\gamma_1$–$\gamma_1$) and ($\gamma_2$–$\gamma_2$) transitions are active in $\pi$-polarization, ($\gamma_1$–$\gamma_3$) and ($\gamma_2$–$\gamma_3$)—in $\sigma$-polarization, and only ($\gamma_3$–$\gamma_3$)—both in $\pi$- and $\sigma$-polarizations. At increasing temperature, $C_1$ distortion, depolarizing the transitions at low temperatures, disappears (while $C_3$ distortion remains, otherwise $\sigma$-polarization would be forbidden), and majority of the transitions are indeed totally $\pi$ or $\sigma$ polarized (see Fig. 1 and Table 1).

Thus, number of absorption lines at low temperature, and the character of their polarization both at low and high temperatures prove, that the local symmetry of the ion $Tm^{3+}$ environment in the crystal $TmAl_3(BO_3)_4$ is $C_3$ and it decreases to $C_1$ at a low temperature. Effective selection rules and polarizations of lines at high enough temperatures (when the line-width is larger than the splitting in $C_3$ symmetry) have been obtained. In the light of said above, it is possible to affirm, that the local symmetry of $Tb^{3+}$ and $Nd^{3+}$ in the identical crystal [2–4] is also lower than $D_3$, since spectra of $f$–$f$ transitions are observed in both polarizations.

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